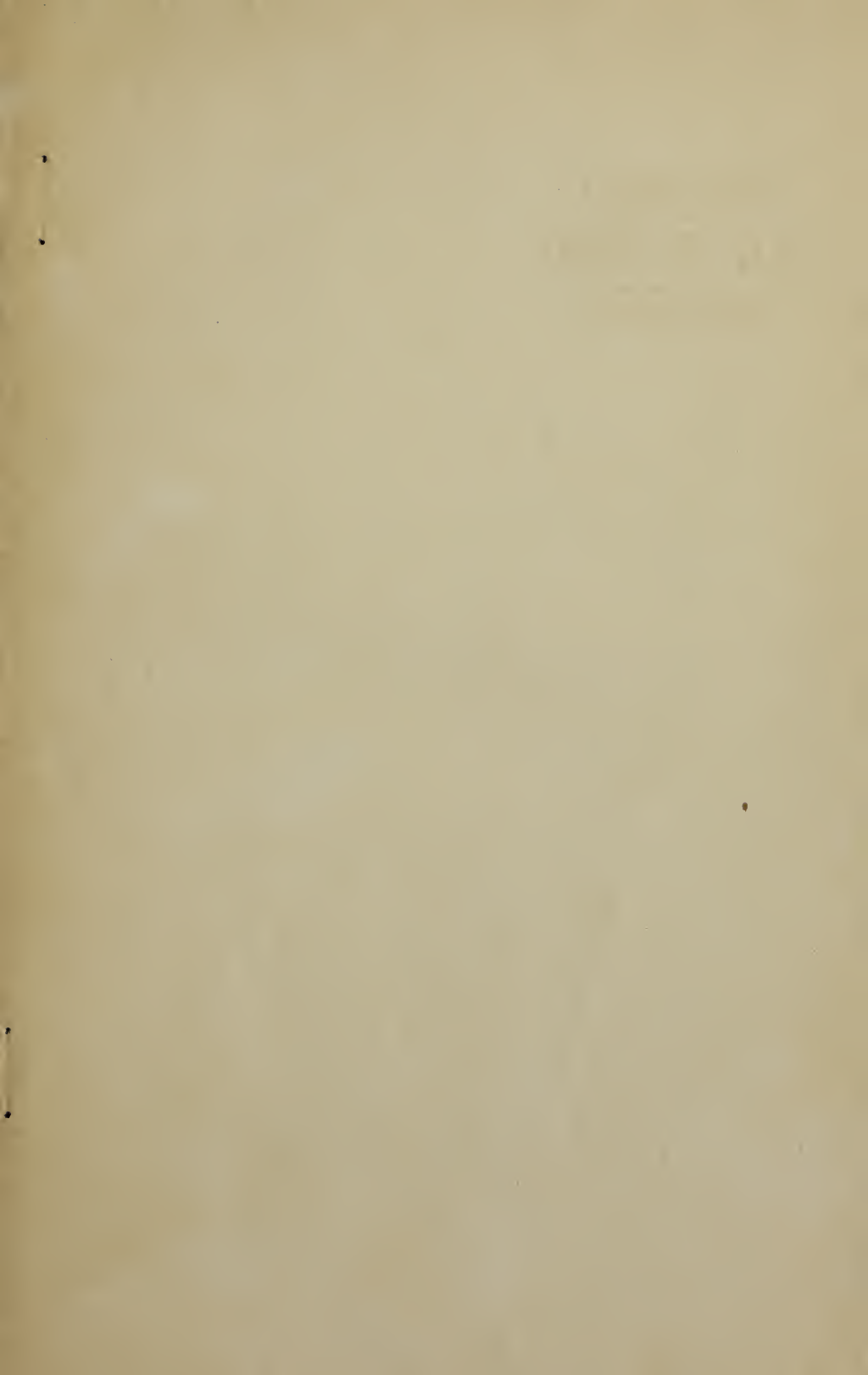


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By O. F. Tower.

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THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC SUBSTANCES CONTAINING NITROGEN.

By O. F. TOWER.

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IN determining carbon and hydrogen in substances containing nitrogen, use is commonly made of a metallic copper spiral at the exit end of the combustion tube to reduce oxides of nitrogen. Liebig was the first to observe that such oxides might be formed, and he showed that the amount of nitric oxide formed, when determining nitrogen by heating with copper oxide, was sufficient to vitiate the results.¹ He further showed that no appreciable quantities of other oxides of nitrogen could be formed, for when the quantity of nitrogen collected was increased by the amount of nitrogen in the nitric oxide produced, the correct percentage of nitrogen in the substance was obtained. Later Klingemann² determined the amount of nitric oxide formed from a variety of complex nitrogen-containing substances, when nitrogen is determined by burning with copper oxide according to the method of Frankland and Armstrong. His results show that the quantity of nitric oxide produced is usually very small, from 0.00 to 0.28 cc., occasionally it is more, and in the case of picric acid 0.90 cc. was found. This last equals only 0.0011 gram. The amount of the substance burned was commonly about 0.1 gram. His results show further that the amount of

¹ Pogg. Ann., 18, 357.

² Ber. d. chem. Ges., 22, 3064.

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 nitric oxide formed does not depend on the nature of the substance, nor on the percentage of nitrogen in the substance, and, moreover, it is very variable for different combustions of the same substance. It, however, seems to be somewhat influenced by the rapidity of the combustion. No direct determinations of the amount of nitrogen oxidized seems to have been made in connection with the determination of carbon and hydrogen in substances containing nitrogen. A few combustions of such substances, made at the time work on a former article¹ was in progress, seemed to show that no appreciable quantities of oxides of nitrogen could be formed, and that, consequently, a metallic copper spiral was unnecessary, particularly in the case of those substances where the nitrogen was in the amidic form. The following work was, therefore, undertaken to determine, if possible, if oxides of nitrogen are formed in such quantity as to interfere with the accuracy of the determinations of carbon and hydrogen, rendering imperative the use of a metallic copper spiral when burning all such compounds.

86 The method of making combustions differed somewhat from that described in the article just cited. No cylinder of compressed oxygen was at my disposal in this laboratory, so that it was necessary to use oxygen prepared in the usual manner and confined in a gas-holder over water. For reasons which will be given later, at the close of most of the combustions the oxygen was swept out by air. The series of absorbing tubes was changed slightly by introducing after the first soda-lime tube a small U-tube containing glass wool drenched with sulphuric acid instead of the tube containing in one side soda-lime and in the other calcium chloride. This change was made for the reason that occasionally a carbon determination came out low. It has been shown by Dibbits² that calcium chloride at ordinary temperature fails to absorb about eight per cent. of the water vapor necessary to saturate the air at the same temperature. In cases where combustions are carried on in an atmosphere of oxygen, so that only a small quantity of gas, comparatively, is aspirated through the system of tubes, the error thus caused is usually small enough to be inappreciable. Where, however, the oxy-

¹ This Journal, 21, 389.

² *Ztschr. anal. Chem.*, 15, 148.

gen is afterwards displaced by air, and consequently the quantity of gas which passes through the system is much greater, a considerable error can result. With this arrangement of tubes there was no certain means of telling when the absorptive power of the soda-lime tube was exhausted. Hence no soda-lime tube was used for more than two combustions.

The substances burned were selected so as to represent different types of bodies containing nitrogen. They were hippuric acid, paratoluidine, urea, dinitrobenzene, nitraniline, and picric acid. Among these are compounds containing amido and nitro groups, some having a large and some a small percentage of nitrogen. The results obtained with the first five will be given first, and afterwards picric acid will be discussed by itself. Only well-crystallized samples of these preparations were employed. Their purity was established by determining the percentage of nitrogen which they contained. All nitrogen determinations were made according to the Kjeldahl method modified to include the nitrogen of nitrates, as adopted by the Association of Official Agricultural Chemists.¹ The determinations were made in duplicate and resulted as follows:

Substance.	Nitrogen.		Theoretical.
	Found.	Found.	
	1.	2.	
	Per cent.	Per cent.	Per cent.
Hippuric acid.....	7.85	7.82	7.82
Paratoluidine	13.05	13.19	13.08
Urea.....	46.58	46.69	46.67
Dinitrobenzene.....	16.62	16.65	16.67
Nitraniline.....	20.33	20.28	20.29

The agreement between the results obtained and the theoretical is such as to show that the substances were sufficiently pure.

The carbon and hydrogen in these compounds was then determined, sometimes using and sometimes without using a copper spiral. If oxides of nitrogen were formed, and no copper spiral were used, these oxides would pass over and, with the exception of nitric oxide, be absorbed in great part by the concentrated sulphuric acid, thereby increasing the apparent weight of absorbed water, and the corresponding percentage of hydrogen. In the first few combustions, in fact, the percentage of hydrogen

¹ Methods of Analysis, Bulletin 46, Division of Chemistry, U. S. Department of Agriculture, p. 17.

was too high, whether or not a copper spiral were used. For example, from the combustion of dinitrobenzene, the following percentages of hydrogen were obtained :

	Per cent.
With copper spiral	2.84
“ “ “	2.62
“ “ “	2.66
Without copper spiral	2.69
“ “ “	2.54
“ “ “	2.75
Theoretical.....	2.38

The inference from these results seemed to be that something rendered the copper spiral ineffective. At the beginning of each of these combustions the tube was filled with oxygen gas, and it was noticed that when a metallic copper spiral was introduced, as it became heated it was immediately oxidized. It is possible that the oxidation was so complete as to prevent the copper having any reducing effect on oxides of nitrogen. To obviate this, at the close of each combustion the oxygen in the tube was swept out by air in the usual manner. With this precaution it could easily be observed that the copper spiral was not oxidized so rapidly as before. The percentage of hydrogen was, however, still too high, varying little from the former results.

In all these combustions the percentage of carbon found was constant and agreed well with the theory. Blank tests at this time showed that the drying train was inadequate, admitting water into the combustion tube. Nothing, therefore, could be inferred from the foregoing results. The sulphuric acid in the drying cylinders was replenished and the number of cylinders increased to three. No further difficulty was then experienced in freeing the entering gases from water. Further combustions now gave a lower percentage of hydrogen, but in the case of substances containing very little hydrogen the results were still somewhat higher than the theory ; no higher, however, than is frequently the case in elementary analysis of compounds of this kind. The results are given below. To avoid the possibility of the copper spiral becoming immediately oxidized and thus proving ineffective, the oxygen was in every case swept out with air.

Substance.	Copper spiral.	Amount used.	Amount CO ₂ found.	Carbon		Amount H ₂ O found.	Hydrogen	
		Gram.	Gram.	Found. Per cent.	Theor. Per cent.	Found. Gram.	Found. Per cent.	Theor. Per cent.
Hippuric acid..	with	0.2017	0.4464	60.37	60.34	0.0915	5.08	5.03
	"	0.2057	0.4558	60.31		0.0937	5.10	...
	without	0.1895	0.4176	60.11		0.0860	5.08	...
	"	0.2045	0.4521	60.30		0.0937	5.13	...
	"	0.2032	0.4485	60.21		0.0930	5.12	...
Paratoluidine .	without	0.1912	0.5498	78.44	78.50	0.1452	8.50	8.41
	"	0.1821	0.5242	78.52		0.1369	8.41	..
Urea.....	with	0.2011	0.1472	19.97	20.00	0.1210	6.73	6.67
	"	0.2031	0.1490	20.01		0.1243	6.85	...
	"	0.2119	0.1565	20.15		0.1291	6.82	...
	without	0.2028	0.1487	20.00		0.1240	6.84	...
	"	0.2116	0.1560	20.11		0.1288	6.81	...
	"	0.2006	0.1471	20.00		0.1204	6.72	...
	"	0.2052	0.1498	19.91		0.1245	6.79	...
Dinitrobenzene.	with	0.2194	0.3444	42.82	42.86	0.0482	2.46	2.38
	"	0.2200	0.3467	42.98		0.0496	2.42	...
	without	0.2161	0.3400	42.92		0.0486	2.52	...
	"	0.2108	0.3311	42.84		0.0446	2.37	...
Nitraniline	"	0.1750	0.3348	52.19	52.17	0.0702	4.49	4.35
	"	0.1782	0.3412	52.23		0.0701	4.40	...

On comparing the results with and without the use of a copper spiral, there is no ground for assuming the formation of oxides of nitrogen. These results were not, however, considered sufficient proof that no such oxides are formed.

As was stated before, any such oxides, with the exception of nitric oxide,¹ would be retained by concentrated sulphuric acid. The sulphuric acid in the first U-tube was, therefore, examined for nitrogen by the Kjeldahl process. The solution of hydrochloric acid used in this work was approximately seminormal, ten cc. containing 0.1845 gram pure acid. The standard ammonia solution was about one-sixth the strength of the acid, ten cc. being equivalent to 0.01200 gram nitrogen. The ammonia solution gradually became weaker on standing, so that its strength in terms of the standard acid was determined each day it was used. Blank determinations were first made to see if the reagents employed were free from nitrogen. Four cc. hydrochloric acid were used in each determination, and the titrations with ammonia were 23.30, 23.18, 23.10, and 23.26 cc., respect-

¹ Nitric oxide is not absorbed by concentrated sulphuric acid. See *J. Soc. Chem. Ind.*, 1885, 178; *Ber. d. chem. Ges.*, 18, 1391; *Chem. News*, 55, 28.

ively, average 23.21 cc. Had the reagents contained no nitrogen, the quantity of ammonia required in each case would be 23.70 cc., which differs from the average by 0.49, or in round numbers 0.50 cc., equivalent to 0.0006 gram nitrogen. Allowance was made for this in all the following determinations. The sensitiveness of the method can also be seen from the above figures. The greatest difference between any two titrations is 0.20 cc., equivalent to 0.00024 gram nitrogen, and the greatest variation from the average is 0.11 cc., equivalent to 0.00013 gram nitrogen. By this method, therefore, nitrogen can be determined within 0.0002 gram. This is sufficiently accurate for this work, as the limit of error in weighing a U-tube under changing atmospheric conditions is usually not less than 0.0002 gram. Simple U-tubes were used to absorb the water and not those of the Volhard pattern with a bulb on one arm, as it was desired that all water should be taken up directly by the sulphuric acid. The U-tubes were filled with some of the same acid as that used for the Kjeldahl determinations. After a combustion the contents of these tubes were poured into a digestion flask, and the tubes well rinsed with additional sulphuric acid. The amount of nitrogen in the acid was then determined.

The sulphuric acid used to absorb the water in most of the combustions, whose results are given in the last table, was treated thus, but no traces of nitrogen could be found. This was surprising, for it was confidently expected that not negligible quantities of nitrogen were oxidized, particularly in the case of nitro bodies, as nitraniline and dinitrobenzene. Several combustions were then made with these two substances, using the same sulphuric acid to absorb the water from two, and sometimes from three, separate combustions. This acid was then examined for nitrogen, but none was found. Soda-lime will absorb all oxides of nitrogen except perhaps nitric oxide.¹ If, therefore, any of the other oxides of nitrogen should escape absorption by the sulphuric acid, they would certainly be absorbed by the soda-lime. The soda-lime which had been used in several combustions of nitraniline and dinitrobenzene was, consequently, treated with concentrated sulphuric acid in a flask,

¹ Nitric oxide is not absorbed by strong alkalies. See *J. Chem. Soc.*, (1877), 2, 37; Wien: *Monatshefte*, 13, 86.

and the mixture distilled until sulphuric acid commenced to come over. This distillate was examined for nitrogen, but none was found. The results of all these determinations were very similar to those obtained in the blank tests. An example will suffice.

SUBSTANCE BURNED, DINITROBENZENE.

	cc.
Hydrochloric acid used in each case.....	3.00
Theoretical amount of ammonia to neutralize, allowance being made for nitrogen in reagents.....	17.40
Actual amount of ammonia used in each titration (substance examined for nitrogen):	
Sulphuric acid from one combustion.....	17.48
“ “ “ two combustions.....	17.37
“ “ “ three combustions.....	17.50
Distillate from soda-lime, two combustions	17.42

In other cases titrations were obtained running from 17.32 to 17.50 cc., the former being the lowest figure ever observed, so that it is safe to draw the inference, that no appreciable quantities of oxides of nitrogen which are absorbed either by concentrated sulphuric acid or soda-lime were formed.

Small quantities of nitric oxide may have been formed, as this gas would pass the sulphuric acid and soda-lime without being absorbed, and consequently would not affect the determinations of carbon and hydrogen. Of course, if it came in contact with oxygen in the tube, it would immediately become oxidized, and then could be readily absorbed. In making a combustion there was, however, little opportunity for oxidation. At the beginning of a combustion the tube was full of air. During the preliminary heating of the substance no air or oxygen was aspirated through the system, so that the oxygen of the contained air would very soon either be used up or driven out by the production of carbon dioxide and other gases. Only after the substance was completely charred and there was no further bubbling of gas through the sulphuric acid of the water-absorbing tube, was the aspiration of oxygen commenced. From Klingemann's results it would be inferred that some nitric oxide might be formed, but in any event very little. It may be remarked that no red fumes were ever noticed where the unabsorbed gases

finally escaped into the air, although under somewhat different circumstances such fumes have been observed by others.¹

The results with picric acid will now be given. With this substance Klingemann² obtained much more nitric oxide than with any other substance which he used.

DETERMINATION OF CARBON AND HYDROGEN IN PICRIC ACID.

Theoretical values, carbon 31.44 per cent., hydrogen 1.31 per cent.

Combustion number.	Copper spiral.	Amount used. Gram.	Amount carbon dioxide found. Gram.	Corresponding carbon. Per cent.	Amount water found. Gram.	Corresponding hydrogen. Per cent.
1	with	0.1551	0.1793	31.53	0.0208	1.50
2	"	0.1551	0.1786	31.41	0.0201	1.45
3	without	0.1605	0.1875	31.86	0.0250	1.75
4	"	0.1613	0.1894	32.03	0.0266	1.85
5	"	0.1512	0.1771	31.95	0.0210	1.55
6	"	0.1614	0.1881	31.79	0.0244	1.69
7	"	0.1595	0.1866	31.91	0.0229	1.61

DETERMINATION OF NITROGEN IN THE SULPHURIC ACID AND SODA-LIME USED IN THE PREVIOUS COMBUSTIONS.

Hydrochloric acid used each time 3.00 cc., equivalent to 17.40 cc. ammonia.³

Combustion number.	Sulphuric acid.			Soda-lime distillate.		
	Titration. cc.	Difference. cc.	Nitrogen. Gram.	Titration. cc.	Difference. cc.	Nitrogen. Gram.
2	17.35	...		17.42	...	
3	16.85	0.55	0.0007	17.05	0.35	0.0004
4	16.30	1.10	0.0013	16.75	0.65	0.0008
5	17.25	0.15	0.0002	16.90	0.50	0.0006
6	17.20	0.20	0.0002 }	16.55	0.85	0.0010
7	17.22	0.18	0.0002 }			

From the first table it will be seen that the results, when no copper spiral was used, not only in almost every case are higher than the results with the copper spiral, but they also do not agree so well with the theory. The second table shows that some nitrogen was found both in the sulphuric acid and in the soda-lime when no copper spiral was used, which proves that small quantities of one or more of the oxides of nitrogen were formed and absorbed by these reagents. The nitrogen determinations of combustion 1 were lost. There is, however, no reason to suppose they would have differed materially from those

¹ Zincke and Kegel: *Ber. d. chem. Ges.*, 23, 246.

² 0.90 cc., equivalent to 0.0011 gram NO from about 0.1 gram picric acid. *Ber. d. chem. Ges.*, 22, 3069.

³ Allowing for nitrogen in reagents. In this table the columns headed "Difference" give the differences between 17.40 and the numbers in the columns immediately preceding.

of 2, which showed no nitrogen was present. In combustion 4, the substance was introduced while the tube was quite warm. Shortly after closing the tube a slight explosion took place. As the stoppers were not blown out, the combustion was completed. The explosion probably accounts for the larger amount of nitrogen found in this case. In 6 and 7, the same soda-lime was used for both. The amount of nitrogen obtained from it, therefore, resulted from two combustions.

To show whether or not these amounts of nitrogen account approximately for the high percentages of carbon and hydrogen when no copper spiral was used, these percentages have been recalculated in combustions 3, 4, and 5, on the hypothesis that the nitrogen was absorbed as nitrogen peroxide, NO_2 . As will be observed, making this allowance causes the results to agree substantially with those when a copper spiral was used.

RECALCULATION OF PERCENTAGES OF CARBON AND HYDROGEN IN
PICRIC ACID.

Combustion number.	NO_2 corresponding to N found in H_2SO_4 . Gram.	Corrected hydrogen. Per cent.	NO_2 corresponding to N found in soda- lime. Gram.	Corrected carbon. Per cent.
3	0.0020	1.60	0.0013	31.65
4	0.0040	1.57	0.0023	31.63
5	0.0006	1.51	0.0018	31.57

The effect of burning picric acid, using a copper boat, was tried with the hope that it would completely reduce any oxides of nitrogen. In some instances the picric acid was also mixed with powdered copper oxide. In every case, however, an explosion of considerable violence occurred, no matter how gradually the tube was heated, so that no results could be obtained.

To show that the Kjeldahl method is accurate for determining small amounts of nitrogen existing in the nitro condition, the results obtained from analyzing very small quantities of dinitrobenzene are given.

NITROGEN DETERMINATIONS WITH DINITROBENZENE.

Amount used.	Hydro- acid used.	Ammonia to chloric neutralize, allowing for N in reagents.	Titration obtained.	Differ- ence.	Correspond- ing nitrogen.	Theoretical nitrogen in substance taken.
Gram.	cc.	cc.	cc.	cc.	Gram.	Gram.
0.0100	3.00	17.40	16.05	1.35	0.00162	0.00167
0.0100	3.00	17.40	15.92	1.48	0.00177	0.00167
0.0050	3.00	17.40	16.80	0.60	0.00072	0.00083
0.0050	3.00	17.40	16.65	0.75	0.00090	0.00083

This shows conclusively that this method is well adapted to the purpose for which it has been used in this work.

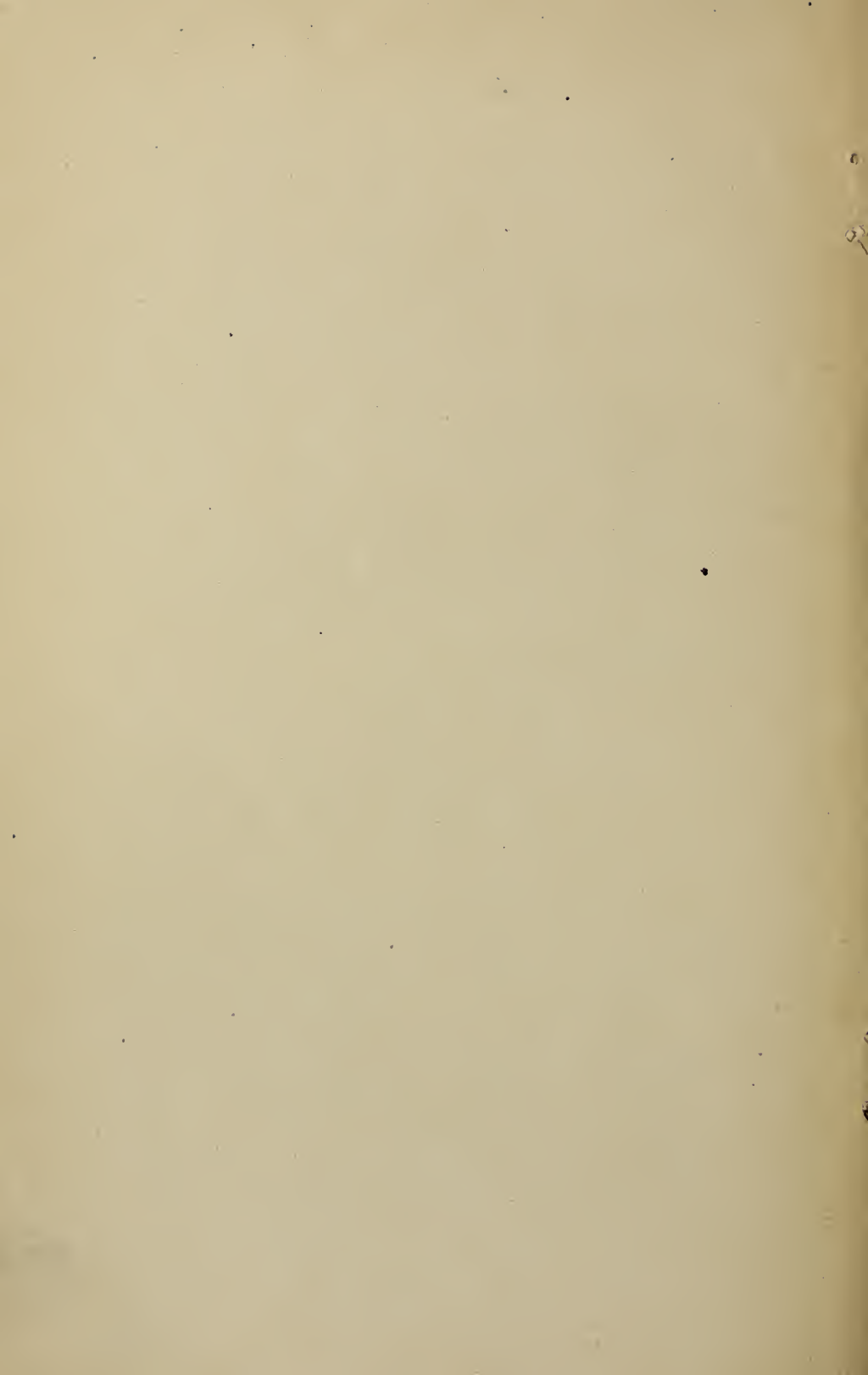
The results of this investigation may be summed up as follows :

Amido compounds, of which urea, hippuric acid, and paratoluidine were taken as types, yield no oxides of nitrogen absorbed by concentrated sulphuric acid or by soda-lime. It is, therefore, not necessary to use a copper spiral when burning them.

Of the nitro substances burned, nitraniline, dinitrobenzene, and picric acid, only the last gave oxides absorbed by the reagents. Judging from the increase in weight of the absorbing tubes, the nitrogen was probably for the most part absorbed as nitrogen peroxide.

Nitric oxide may have been produced to a limited extent in any of the combustions. For, unless this oxide is further oxidized, it is not absorbed by either concentrated sulphuric acid or soda-lime, and consequently has no effect on the accuracy of the determination of carbon and hydrogen.

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